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Fatty acids and antioxidant effects on grease microstructures☆

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Abstract

The search for biobased material as industrial and automotive lubricants has accelerated in recent years. This trend is primarily due to the nontoxic and biodegradable characteristics of seed oils that can substitute mineral oil as base fluid in grease making. The paper discusses the preparation of lithium soap-based soy greases using different fatty acids and the determination of crystallite structure of soap using transmission electron microscopy (TEM). Lithium soaps with palmitic, stearic, oleic, and linoleic acids were synthesized and mixed with soybean oil (SBO) and additives to obtain different grease compositions. TEM measurements have revealed that the soap crystallite structure impact grease consistency. Soap fiber length and their cross-linking mechanism in the matrix control grease consistency (National Lubricating Grease Institute (NLGI) hardness, ASTM D-217 method). Lithium stearate-based soy grease has a relatively more compact fiber structure than Li palmitate. Linoleic acid (C_{18}, = =) with two sites of C–C unsaturation in the chain has a much thinner and more compact fiber network than oleic acid (C_{18}, =). The presence of additive in grease produces a soap with looser network and larger fiber structure than similar grease containing no additive. A close analysis of grease microstructure will help in the development of better performing grease for industrial applications.

Keywords: Vegetable oils; Li grease; Fatty acids; Transmission electron microscopy; Fiber structure

1. Introduction

Vegetable oil-based greases are semi-solid colloidal dispersions of a thickening agent (a metal soap) in a liquid lubricant matrix (vegetable oil). Grease is the preferred form of lubrication in hard-to-reach places in a mechanically rubbing or dynamic systems. Grease acts as reservoir for lubricant-based fluids and additive molecules. Much of its functional properties are dependent on their ability to flow under force, have shear stability, resist viscosity changes with temperature and pressure, water stable, seal out contaminants, decrease dripping and spattering, etc. The dependability of lubricating grease depends on their physical properties that are structurally related, which is obtained by the proper selection of ingredients and processing. Thus, it is pertinent to understand the grease microstructure as it contributes significantly

☆ Names are necessary to report factually on available data; however, the USDA neither guarantees nor warrants the standard of the product, and the use of the name by USDA implies no approval of the product to the exclusion of others that may also be suitable.

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to various functional properties of grease. Grease consistency (or National Lubricating Grease Institute (NLGI) hardness, ASTM D-217 method, 2000) is largely dependent upon the thickener fiber structure and its distribution in the grease medium. The performance properties of grease are primarily dependent on their ability to provide lubrication to mechanically operating moving parts by supplying base oil as a thin film separating the metallic surfaces and also removing heat and wear debris from the friction zone. The physical and chemical degradation of grease during use (Carré et al., 1983; Araki et al., 1995) and failure of various mechanical parts due to inadequate lubrication (Cann and Lubrecht, 1999) have been reported.

Several mechanisms have been proposed on timed lubricant release and replenishment of starved lubricant sites during operation. Laboratory simulations range from simple thermal stability tests to more complex lubrication measurements (Aihara and Dowson, 1978; Zhu and Neng, 1988; Williamson, 1995). However, a model of this mechanism resulting in stable lubricant film formation in concentrated metal contact has not been established and requires more experimental findings.

Unpublished data show that the fatty acid chain length and C–C unsaturation influence soap fiber structure and their networking mechanism. Therefore, an understanding of fiber growth and their network structure in grease matrix is required to relate base oil holding capacity and oil release by shear degradation of soap thickener during operation to additive compatibility, bleed resistance, viscosity, thermal stability, texture, and appearance. Critical physiochemical properties are therefore dependent on the consistency of grease and their behavior in the mechanical system. Controlling the growth and distribution of soap fiber during grease manufacturing processes can result in products with the desired physical, chemical, and performance properties.

2. Materials and methods

2.1. Materials

Alkali refined soybean oil (SBO) from Pioneer Hi Bred Intl. Inc. (Des Moines, IA) was used as the base fluid. The oil has the following fatty acid composition determined by gas chromatographic analysis (AACC 58-18, 2000) in percentage: $C_{16:0} = 6$; $C_{18:0} = 5.5$; $C_{18:1} = 22.0$; $C_{18:2} = 66.0$; and $C_{18:3} = 0.5$. This oil shows much lower linolenic content (0.5%) than regular soy oil (≈8%). The lower linolenic acid moiety in the fatty acid chain results in a significant improvement in the thermo-oxidative stability of vegetable oil structure. Lithium hydroxide monohydrate ($LiOH{\cdot}H_2O$, 98%), palmitic (90%), stearic (95%), oleic (90%), and linoleic acids (90%) were obtained from Aldrich (Milwaukee, WI) and were used without any further purification.

2.2. Additive

Antimony dithiocarbamate used as an antioxidant and extreme pressure additive was obtained from R.T. Vanderbilt Co. Inc. (Norwalk, CT). Additive was added at 0–8% by weight of the total formulation.

2.3. Grease preparation

A mixture of $LiOH{\cdot}H_2O$, fatty acid (taken in 1:0.75 to 1 equivalent ratio with the Li-based material), and SBO (in equivalent weight ratio of the metal–acid mixture) were uniformly mixed with a mechanical stirrer at 90 °C in a 3 l wide-mouth glass reactor. The temperature was then slowly raised to 190 ± 2 °C and maintained for 3 h with stirring. After the cooking period, the mixture was allowed to cool; and at 150 °C, an additional amount of SBO (60–80% of the total reaction mixture) and additive (0–8 wt.% of the total reaction mixture) were added. The final mixture was allowed to cool to room temperature to obtain the grease. The resulting grease was milled using 3-roll mill equipment. During this process, grease was passed through the rollers thrice until it was thoroughly homogenous and the particle size reached 2–3 μm. The final product had a smooth, paste-like texture. Similar procedure was used to prepare the other greases made with varying composition of base oil, fatty acid, lithium hydroxide, and additive.

2.4. Transmission electron microscopy (TEM)

The grease samples were diluted with water and one drop of grease solution was added with a pipette onto a carbon film of copper grid. Philips EM 400 was

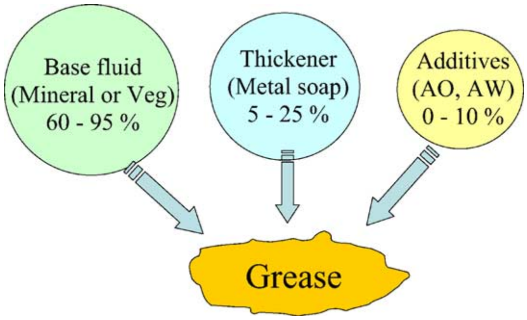


Fig. 1. Typical composition of grease.

employed to obtain bright field images of grease samples at 120 kV. The Li particles in the oil matrix were specifically imaged in order to characterize the shape, size, and dispersion of the grease as a function of experimental conditions (Mansot, 1989; Kimura et al., 2001).

3. Results and discussion

Lubricating greases are semisolid or solid colloidal dispersions owing their consistency to a gel-type network. A typical composition of grease includes base fluids, thickener, and additives (Fig. 1). The base fluid is contained and stabilized in the matrix by the fiber structure of the soap molecules. Metals usually used in the soap composition include lithium, calcium, sodium, aluminum, and titanium. The fatty acids include stearic, oleic, linoleic, and linolenic. Although, it is known that the general structure of the soap phase in grease consists of crystallites, which take the form of fibers, this does not clearly explain why a small amount of solid (soap) could immobilize a large volume of the base oil in grease. These fiber structures form a complex network that traps the base oil molecules in two ways: (i) by direct sorption of the oil by polar ends of soap molecule and (ii) penetration of base oil in the interlacing structure of soap fiber. The oil retaining property of grease may be due to the attractive influence of soap fibers extending through many layers of base oil molecule and not to the swelling of the fibers (Browning, 1950). Therefore, the physical and chemical behavior of grease is largely controlled by the consistency or hardness, which is dependent upon the microstructure of soap fibers.

The base fluid used in this study is soybean oil. The oil is a triacylglycerol molecule with fatty acid chains mainly composed of oleic ($C_{18:1}$), linoleic ($C_{18:2}$), and linolenic ($C_{18:3}$) moieties. Each triacylglycerol molecule has three ester linkages and unsaturations depending on the distribution of fatty acid moieties (Fig. 2). The presence of polar group with a long hydrocarbon chain makes vegetable oil amphiphilic allowing them to be used as boundary lubricants. The molecules have strong affinity for and interact strongly with metal surfaces. The long hydrocarbon

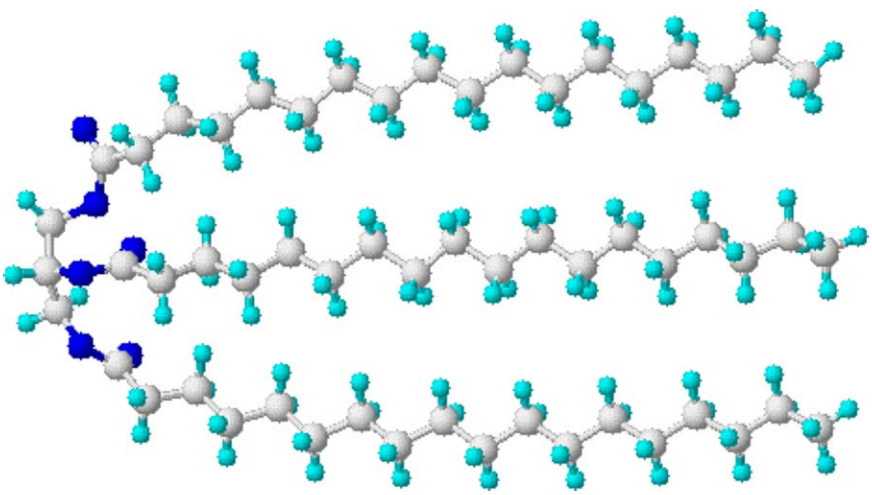


Fig. 2. Triacylglycerol molecule. Dark circles are oxygen atoms of the ester groups.

Table 1
Composition and NLGI hardness of lithium-based soy grease

Fatty acid	Metal[a]:fatty acid ratio	Metal soap:oil[b] ratio	NLGI hardness[c]	Antioxidant (wt.%)[d]
Palmitic	1:1	1:3	2	–
Stearic	1:1	1:3	2–3	–
Stearic	1:1	1:3	2–3	4
Oleic	1:1	1:3	2–3	–
Linoleic	1:1	1:3	1	–

[a] Lithium compound (lithium hydroxide monohydrate) in equivalent ratio with acid.
[b] Ratio of lithium soap of different fatty acids and soybean oil.
[c] ASTM D-217 method.
[d] Antimony dithiocarbamate.

chain is oriented away from the metal surface to form a monomolecular layer with excellent boundary lubrication properties. When the molecule is adsorbed on the metal surface, two types of interactions occur. The adhesive interaction between the ester group and metal is very sensitive to the type and number of functional groups. The lateral interaction caused by dipole–dipole and dispersive interaction between the hydrocarbon chains is sensitive to structural properties including chain length, unsaturation, and stereochemistry (Jahanmir and Beltzer, 1986a, 1986b). Similarly, the nature of fatty acid in the soap structure of grease has a significant influence on the physical and chemical properties. In the current study using transmission electron microscopy (TEM), we observed the formation of dispersiod structure with compact network with an increase in the chain length of the fatty acid in lithium soap. With more interlocking resulting from the long chain fiber structure, increased interactions with base oil in the matrix can be achieved. Grease developed under such condition shows high consistency resulting in higher hardness. The composition and NLGI hardness of lithium-based greases prepared with different fatty acids are listed in Table 1.

The TEMs of palmitic [$CH_3(CH_2)_{14}COOH$] and stearic [$CH_3(CH_2)_{16}COOH$] acids used in the lithium soap to develop soybean oil-based grease are shown in Fig. 3a and b, respectively. Under similar magnification (1.81 μm), Li stearate-based soy grease shows a relatively more compact fiber structure than Li palmitate. This is also evident from the NLGI hardness of grease presented in Table 2 (more hardness is represented by higher numerical value). It appears that such compact mesh structure can hold relatively larger amounts of base fluid in the soap matrix due to the excellent interaction. This increases the ability

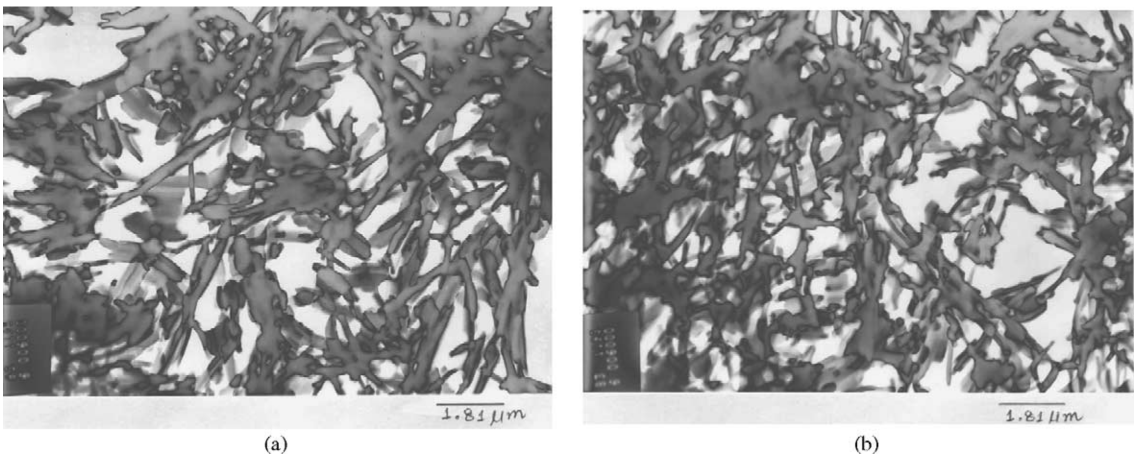


Fig. 3. Effect of fatty acid chain length on the soap fiber structure: (a) Li palmitate soap and (b) Li stearate soap.

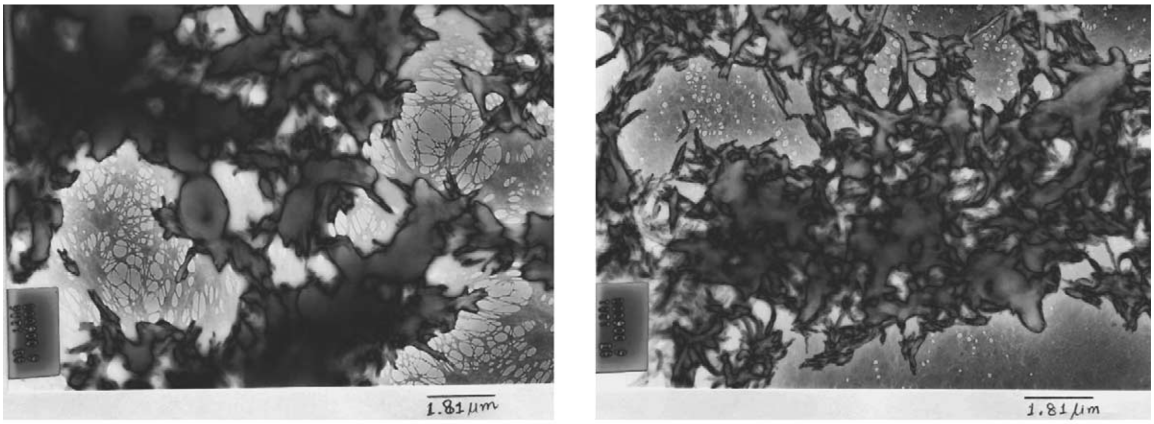
Table 2
NLGI grease classification

Grade number	ASTM penetration (ASTM D 217)
000	445–475
00	400–430
0	355–385
1	310–340
2	265–295
3	220–250
4	175–205
5	130–160
6	85–115

of the grease to resist deformation with increasing fiber length because a long fiber can make more contacts with neighboring fibers than a short fiber with the same diameter. It may be noted at this stage that during extreme shear stress; when a fiber breaks into smaller fragments, the consistency will decrease, whereas when they split into thinner fragments, the consistency will increase. Therefore, the hardness of grease as a result of soap structure can affect oxidation stability, water washout, oil bleeding at higher temperature, and lubricity (Kernizan and Pierman, 1998; Hurley and Cann, 1999).

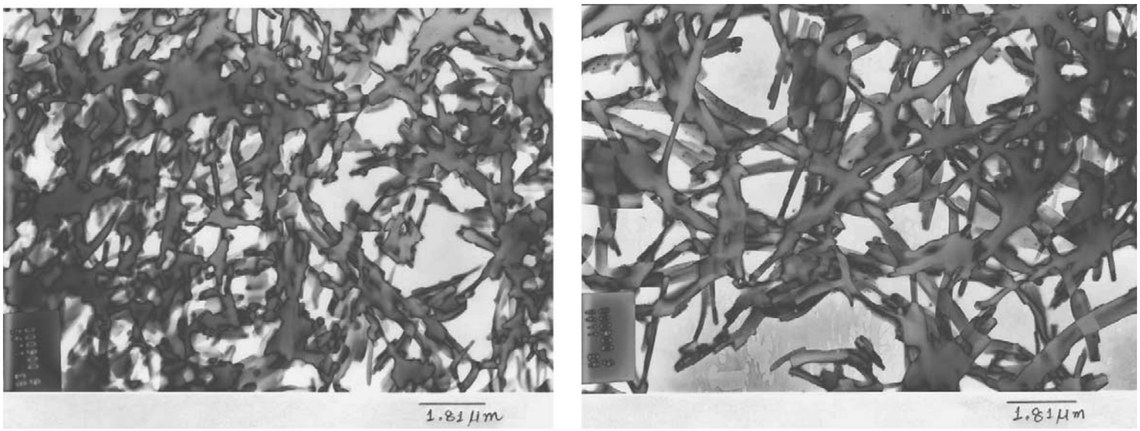
Unsaturation in the fatty acid structure of soap molecule has significant impact on the grease fiber structure. Linoleic acid (C_{18}, = =) (Fig. 4b) with two sites of C–C unsaturation in the chain shows a much thinner and compact fiber network than oleic acid (C_{18}, =) (Fig. 4a) in the soap composition. Excessive thinning of the fiber strand may result in softer grease due to weak mesh structure that is unable to hold the base oil in the grease matrix. Furthermore, the presence or absence of C–C unsaturation with the same chain length acids (Figs. 3b and 4b) in the soap structure results in a distinct difference in the shape and distribution of the fibers. With process parameters and composition remaining the same, and with a decrease in the soap fiber length, there is a tendency to form softer grease (Boner, 1954). Because the growth of soap fibers in the grease matrix is a result of fusion and solidification of adjoining short fibers, this phenomenon is also controlled to a large extent by the procedure used to manufacture grease (Yamamoto et al., 1997). Soap molecules with oleic acid show a comparatively larger fiber structure than linoleic acid. This is also supported from the NLGI hardness of the greases developed (Li oleate soap: NLGI grades 2–3; Li linoleate soap: NLGI grade 1) with similar composition and synthesis procedure (see Table 1).

Additives are usually introduced during the cooling phase of grease making and they remain dispersed in the matrix. These additives are found to enhance some of the functional properties of the base oil in the grease such as oxidation, load-bearing, anti-wear, anti-corrosion, and anti-rust (Stempfel, 1998; Mittal et al., 1998; Fish, 1999; Hunter and Baker, 2000). Due to the presence of additives, the soap thickener structure can be influenced to a large extent by either changing the solubility of the soap in the base oil or



(a) (b)

Fig. 4. Effect of C–C unsaturation in the fatty acid chain on the soap fiber structure: (a) Li oleate soap and (b) Li linoleate soap.



(a) (b)

Fig. 5. Effect of additive on the fiber structure of soap: (a) Li stearate soap and (b) 4 wt.% additive doped in Li stearate soap.

influencing its crystallization. Similarly, the optimum condition for fiber growth through crystallization may vary with different additives. It is believed that the additive molecules are first bound to the soap fibers and the chains attached to additives hold the oil. The TEMs (Fig. 5a and b) show the effect of antimony dithiocarbamate additive on Li stearate soap structure. Under magnification (1.81 μm), the additive doped grease has a looser network structure with larger fibers than the non-additive doped grease with similar metal, fatty acid, and base oil composition (see Table 1). It may be noted, however, that due to the presence of additive molecules, grease hardness is not altered significantly as a result of changes in the soap fiber length and their distribution in the matrix.

4. Conclusions

The effect of fatty acid on grease micro structure was studied with the help of transmission electron microscope. TEM measurements revealed that the soap crystallite structure impact grease consistency. The various performance characteristics of grease in automotive and industrial applications are dependent on hardness, and this can be traced to grease composition and soap fiber structures. Unsaturation and fatty acid chain length of soap molecule dictate the fiber shape and distribution, which can be translated to hardness, thermo-oxidative stability, shear stability, water tolerance, and other important properties of grease. The Li stearate-based soy grease has a relatively more compact fiber structure than Li palmitate. The linoleic acid (C_{18}, = =) with two sites of C–C unsaturation in the chain exhibits a much thinner and more compact fiber network than oleic acid (C_{18}, =). The presence of additive in grease gives a soap with looser network and larger fiber structure than similar grease with no additive. Transmission electron microscopy gives a more defined soap structure with respect to changes in the fatty acid composition and additive concentration. Therefore, optimal selection of fatty acids in soap is required to control the fiber length-to-diameter ratio as well as the extent of fiber cross-linking that stabilizes the base oil in grease.

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